



Short communication

High catalytic activity of anatase titanium dioxide for decomposition of electrolyte solution in lithium ion battery



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HIGHLIGHTS

- Anatase TiO₂ possesses high reactivity to initiate the decarboxylation reaction of electrolyte solution.
- The ROLi species and the new phase of flake-like Li₂TiF₆ material are formed as the reaction products.
- The high reactivity restricts the applications of anatase TiO₂ anode in lithium ion battery.

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ABSTRACT

It has been indicated that anatase TiO₂ is a promising anode material for lithium ion power battery from many previous researches. Whereas, in this work, we find that the anatase TiO₂, when used as an anode for lithium ion battery, has high catalytic activity to initiate the decarboxylation reaction of electrolyte solution, resulting in the large generation of sole gaseous component, CO₂. The ROLi species and the new phase of flake-like Li₂TiF₆ material are the main reaction products between anatase TiO₂ and LiPF₆ based electrolyte solution. This work provides important and urgent information that the surface chemistry of anatase TiO₂ used as the anode material of lithium ion battery must be modified to suppress its catalytic activity for the decomposition of solvents.

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1. Introduction

Anatase titanium dioxide (TiO₂) has been widely investigated as an anode material of lithium ion battery because of its low cost, high stability, abundance and non-toxicity [1–4]. More importantly, the anatase crystal framework is free from volume variation as compared to other transition metal oxides during lithiation/delithiation process [5]. In addition, it is believed that a thermally unstable solid–electrolyte interface (SEI) film cannot be formed on the TiO₂ surface because the lithium ion insertion voltage of anatase TiO₂ is approximately 1.7 V versus Li⁺/Li and its cut-off discharge potential is 1.0 V, which is higher than the reduction potential of most electrolytes or solvents [6].

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Unfortunately, the low electrical conductivity ($\sim 10^{-13}$ S cm⁻¹) of TiO₂ results in poor rate performance, which restricts its real applications in lithium ion battery [6]. Generally, two routes are proposed to improve its rate performance. The first one is to design and tune its microstructure and morphology, and quite many nanostructures, such as hierarchical and nanoporous structure [3], mesocrystals [4], nanospindles [2] and porous nanorods [1] have been reported. Another one is hybridization with carbon materials to obtain hybrid materials, including mesoporous TiO₂ nanospheres/graphene hybrids [7,8], sandwich-like graphene/TiO₂ nanosheets [6], hierarchical anatase TiO₂ nanosheets/carbon nanotube backbone [9], and self-assembled TiO₂/graphene hybrid nanostructures [10]. These aforementioned materials exhibit superior specific capacities, cycling stability and rate capability, promoting the real applications of anatase TiO₂.

Although the electrochemical performance is largely improved by the above efforts, there is another major challenge for the real application of anatase TiO₂, which is its high chemical reactivity. In

our previous work, we investigated the gassing behavior of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ battery and found that the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has high reactivity with electrolyte solution along with generation of gases such as H_2 , CO_2 and CO [11]. It is well-known that the anatase TiO_2 has high photocatalytic activity for organic pollutant decomposition and hydrogen evolution [7,12]. The anatase TiO_2 may also have high catalytic activity for the decomposition of electrolyte solution of lithium ion battery. Unfortunately, to the best of our knowledge, there are no reports for the investigation of the catalytic reactions between anatase TiO_2 and electrolyte solution. In this communication, we, for the first time, report that the anatase TiO_2 has very high reactivity towards electrolyte solution, which contributes to the decarboxylation reaction of solvents along with a large amount of CO_2 generation.

2. Experimental

In this study, anatase TiO_2 was obtained by sintering the precursor amorphous TiO_2 at 450°C for 8 h. The details of the synthesis route of amorphous TiO_2 can be found elsewhere [13,14]. The reaction activity of TiO_2 towards the electrolyte was investigated as follows. 1.6 g of anatase TiO_2 powder was put into aluminum-plastic laminated film packages, and 4 ml solvent (diethyl carbonate (DEC), dimethyl carbonate (DMC), ethylene methyl carbonate (EMC)) or LiPF_6 -based electrolyte solution (1 M LiPF_6 /EC + DMC + EMC) was added into above packages before sealing of the packages in an argon-filled glove box. The packages were stored at 25 or 50°C for 3 months. The volumes of the packages before and after storage were monitored using the water displacement method. The gases generated under these conditions was extracted from the top of package by an injector and analyzed on a gas chromatograph (Agilent 7890A GC System) using the GB/T 9722-2006 method.

The anatase TiO_2 powder after soaking was washed using EMC to remove the electrolyte and solvents on the surface of the soaked TiO_2 samples and then dried them at 80°C . The X-ray diffraction (XRD) measurements of anatase TiO_2 samples before and after soaking in DEC and electrolyte of 1 M LiPF_6 /EC + DMC + EMC at 50°C for 3 months were conducted using a diffractometer (Rigaku D/max 2500/PC) with $\text{Cu K}\alpha$ radiation. Microstructure and morphology of the TiO_2 before and after soaking were examined using field emission scanning electron microscopy (FE-SEM, HITACHI S4800, HITACHI Co., Japan) and transmission electron microscopy (TEM, JOEL JEM-2100F, Japan). In order to further confirm the reaction product, XPS measurements were conducted using Physical Electronics PHI5802 instrument with X-rays magnesium anode (monochromatic $\text{K}\alpha$ X-rays at 1253.6 eV) as the source. The C 1s region was used as a reference and was set at 284.8 eV. The Fourier transform infrared spectroscopy (FTIR) spectrometer (Bruker VERTEX 70) was applied to further investigate the residual products after reaction.

3. Results and discussion

Fig. 1a shows the detailed XRD patterns of anatase TiO_2 samples before and after soaking in DEC and electrolyte of 1 M LiPF_6 /EC + DMC + EMC at 50°C for 3 months. It is exhibited that the diffraction peaks of the prepared TiO_2 are exclusively ascribed to TiO_2 crystal with the tetragonal anatase phase (JCPDS No. 21-1272). After the soaking in DEC, the XRD patterns of TiO_2 do not show any changes, indicating that the anatase TiO_2 can maintain its original structure. After soaking in electrolyte solution, the strong characteristic peaks of anatase TiO_2 can also be observed, indicating that the main phase of the reacted products is still the anatase TiO_2 and more interesting, a new phase of Li_2TiF_6 (JCPDS file of card No. 24-

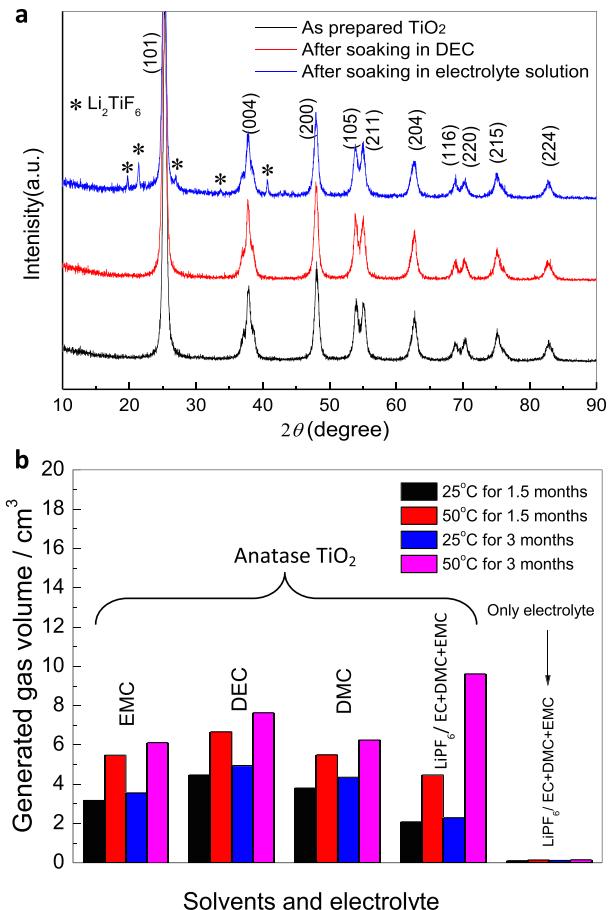


Fig. 1. XRD of the prepared TiO_2 before and after soaking in DEC and electrolyte solution of 1 M LiPF_6 /EC + DMC + EMC at 50°C for 3 months (a) and gas generated volume when anatase TiO_2 is soaked in solvents and electrolyte solution for 1.5 and 3 months (b).

0662) is formed as a result of the reaction between HF and anatase TiO_2 (**Fig. 1a**) [15,16].

Severe gassing behavior occurs when the anatase TiO_2 is soaked in both solvents and electrolyte solution, whereas no obvious gassing behavior appeared when there is only electrolyte solution in the absence of TiO_2 . This difference can be clearly identified from the generated gas volume after reaction (**Fig. 1b**). The above results indicate that the gassing behaviors are intimately related to the anatase TiO_2 . In addition, the solvents of DMC, DEC, and EMC have different molecular structure, which results in their different reactivity with anatase TiO_2 . Therefore, different gas amount was generated when the anatase TiO_2 was soaked by solvents. In particular, up to 9.6 cm^3 of gas was generated after the anatase TiO_2 (1.6 g) was soaked in electrolyte solution (4 ml) at 50°C for 3 months, which is much larger than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and rutile TiO_2 soaked in the same electrolyte at the same condition (0.67 and 0.25 cm^3) [11]. Above results clearly present that the anatase TiO_2 has much higher chemical activity than $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and rutile TiO_2 for the decomposition of solvents reported in our previous work. We also tested the volume of generated gases in packages after storage 1.5 months. Compared to that after storage 3 months, it is found that when the TiO_2 was soaked by single solvent, the generated gases only has minor increase with the storage time increasing from 1.5 to 3 months at both 25 and 50°C , while which has larger increase when the TiO_2 was soaked by electrolyte solution (LiPF_6 /EC + DMC + EMC) at 50°C . This may be because that the LiPF_6 in

the electrolyte solution can be gradually decomposed to form PF_5 at 50 °C, which was accumulated during initial storage process. The accumulated PF_5 as a strong Lewis acid cooperated with anatase TiO_2 can accelerate the decarboxylation reactions of solvents, which results in the larger gas generation of anatase TiO_2 soaked by electrolyte solution than that soaked by single solvent at the later storage process (Fig. 1b) [16,27]. The gases were analyzed by gas chromatograms and the results are summarized in Table S1. It is found that CO_2 is the only component of gas generated when the anatase TiO_2 was soaked in both solvents and electrolyte, which is similar to that of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and rutile TiO_2 soaked at the same condition [11], indicating that similar gassing reactions occurred.

The SEM images of TiO_2 presents that the prepared anatase TiO_2 is composed of agglomerates consisting of very small primary particles with an average size of ~30 nm (Fig. 2a). High-resolution TEM (HRTEM) image indicates that the anatase TiO_2 had a well-defined crystal structure (Fig. 2c). The *d*-spacings of 0.35, 0.24 and 0.19 nm are in agreement with that of the (101), (004) and (200) planes of anatase TiO_2 , respectively. The BET surface area of anatase TiO_2 is $48.17 \text{ m}^2 \text{ g}^{-1}$. After soaking the anatase TiO_2 in electrolyte solution, the anatase TiO_2 further aggregates to form a secondary particle with size of ~500 nm. Interestingly, some new phase of flake-like components are found in the reacted anatase TiO_2 (Fig. 2b), which should be a reaction product between anatase TiO_2 and electrolyte solution. HRTEM image of anatase TiO_2 after reaction also presents a similar flake component and the *d*-spacing of 0.27 nm is in agreement with that of the (112) plane of the Li_2TiF_6 (Fig. 2d). This confirms that the new phase of flake-like material is

Li_2TiF_6 . In addition, the surface of anatase TiO_2 particle after the reaction is covered by a thin layer, which is possibly the products of the reaction between anatase TiO_2 and electrolyte solution (Fig. S1).

Fig. 3d shows that the Ti 2p spectrum of the as-prepared TiO_2 consists of a peak (Ti 2p3/2) at 458.4 eV and another peak (Ti 2p1/2) at 464.1 eV, typical for anatase TiO_2 [17,18]. After soaking (Fig. 3e), the intensity of these peaks decreases greatly and they shift to much higher binding energy than that of the as-prepared anatase TiO_2 , which proves that the reacted TiO_2 particles are covered by the reaction products of TiO_2 and electrolyte solution. The peak of Ti 2p3/2 at 462.6 eV further confirms the formation of Li_2TiF_6 after reaction [19].

The O1s XPS profile of the as-prepared TiO_2 presents a peak at 529.6 eV (Fig. 3f), typical for the anatase TiO_2 . After soaking, the peak at 529.6 eV assigned to TiO_2 shifts to higher binding energy (530.2 eV) (Fig. 3g), which is in accordance with the shift occurred to the Ti2p XPS peaks. The binding energy shift may be related to the charging effects after thermal storage [20–22]. Moreover, four new peaks are observed from the O 1s profile, which are a small peak at 530.8 eV assigned to TiO_2 [23], a peak at 532.4 eV assigned to C–O–C or ROLi species, two peaks at 531.7 and 533.4 eV attributed to the C=O species and the oxygen atom of lithium alkyl carbonates bounding to two carbon atoms (ROCOOLi), respectively [24,25]. From the FTIR spectrum of anatase TiO_2 (Fig. 3b) after reaction with electrolyte solution, the characteristic peaks of Li_2CO_3 (at 866, 1425 and 1500 cm^{-1}) cannot be observed, suggesting that the Li_2CO_3 was not formed during soaking of anatase TiO_2 in electrolyte solution. Therefore, the peak at 531.7 eV in XPS profile is

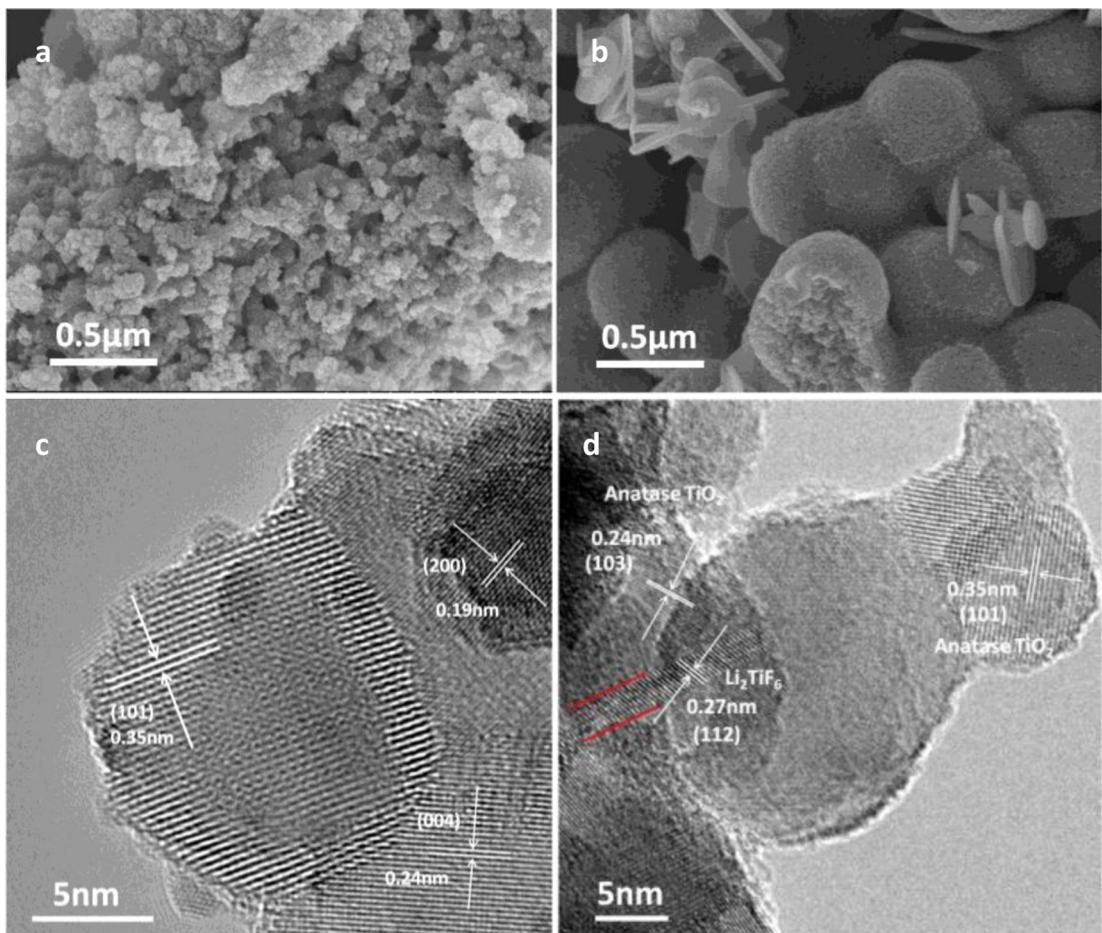


Fig. 2. SEM (a, b) and TEM (c, d) images of the anatase TiO_2 before (a, c) and after (b, d) soaking in electrolyte solution of 1 M $\text{LiPF}_6/\text{EC} + \text{DMC} + \text{EMC}$ at 50 °C for 3 months.

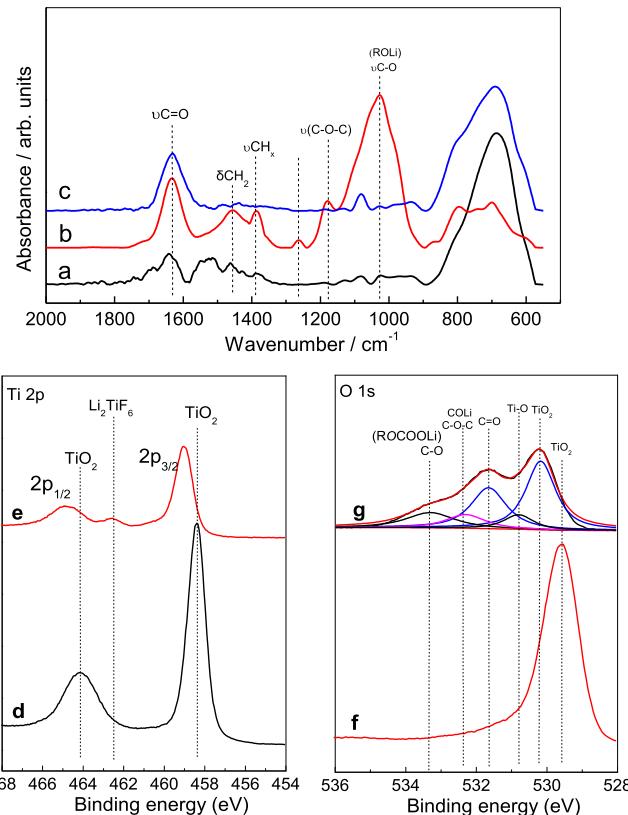


Fig. 3. FTIR spectra of anatase TiO₂ before (a) and after soaking in electrolyte solution (1 M LiPF₆/EC + DMC + EMC) (b) and DEC (c); Ti 2p (d, e) and O 1s (f, g) XPS spectra of anatase TiO₂ (d, f) before and (e, g) after soaking.

not assigned to Li₂CO₃, which may be attributed to the C=O group of ROCOOLi that was also observed in FTIR spectrum (at 1634 cm⁻¹) [24]. Therefore, the C—O—C, ROLi and ROCO₂Li species are the main possible reaction products between TiO₂ and electrolyte solution. The FTIR spectrum of anatase TiO₂ (Fig. 3b) after reaction presents three main peaks at 1634, 1167 and 1024 cm⁻¹, which are associated with C=O, C—O—C and ROLi species respectively, in accordance with the XPS results discussed above. Note that the intensity of ROLi is much larger than that of C=O and C—O—C species, indicating that the ROLi species are the main reaction products between anatase TiO₂ and electrolyte solution.

The gas analyses show that only CO₂ was generated during the soaking reaction and the main reaction products are the ROLi species, which indicate that the decarboxylation reactions of solvents occurs at the interface between anatase TiO₂ and solvents. Since the package solely containing electrolyte solution does not show obviously gassing behavior, suggesting that the gassing reactions are catalyzed by the anatase TiO₂. We also measured the FTIR of TiO₂ that was soaked in the solvent of DEC (Fig. 3c). The C—O—C species cannot be detected, whereas which are found in the TiO₂ sample soaked by electrolyte solution (1 M LiPF₆/EC + DMC + EMC). The TiO₂ initiates the decarboxylation reaction of solvents (such as DEC, DMC, and EMC) that results in formation of CO₂ and ether (such as diethyl ether, methyl ether), which was dissolved in the electrolyte solution. In addition, some residual ether on the surface of TiO₂ sample was washed out by EMC. Therefore, the C—O—C group on the surface of TiO₂ sample soaked by electrolyte solution (1 M LiPF₆/EC + DMC + EMC) may be the (-CH₂—O—CH₂—)_n species that possibly result from the

ring-opening polymerization of EC as reported by some references [26,27], which cannot be dissolved in the electrolyte solution and maintain on the surface of TiO₂ sample. The investigations are ongoing at present to clarify the detailed reaction mechanism.

4. Conclusion

The reactivity of anatase TiO₂ with LiPF₆ based electrolyte and solution was investigated in this work. It is found that the anatase TiO₂ used as an anode material of lithium ion battery is reported here to possess high reactivity to initiate the decarboxylation reaction of electrolyte solution along with substantial CO₂ generation. The anatase TiO₂ can maintain its original structure, while the ROLi species and the new phase of flake-like Li₂TiF₆ material are formed as the reaction products of anatase TiO₂ with LiPF₆ based electrolyte. The high reactivity restricts the applications of anatase TiO₂ anode in lithium ion battery. Based on this point, for the anatase TiO₂ applicable in a real battery, surface modification is urgently required to suppress its catalytic activity for the decomposition of electrolyte solution, which is intimately related to the gassing of battery.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.06.068>.

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